

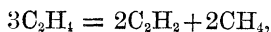
November 2, the flow was never less than 3,000 millions of gallons per day, and on November 2 it reached 4,240 millions. Again, on the 17th the flow was 3,305 millions, and on the 18th, 4,165 millions. It then gradually decreased to 1,845 millions on the day when the sample was drawn. Thus the Thames basin had been twice very thoroughly washed out immediately before the time when the November sample was taken. There had previously been no such floods after the 5th of January in that year. This condition of things affords a fairly satisfactory explanation of the anomalous result yielded by this sample.

III. "The Cause of Luminosity in the Flames of Hydrocarbon Gases." By VIVIAN B. LEWES, Professor of Chemistry at the Royal Naval College, Greenwich. Communicated by Professor THORPE, F.R.S. Received February 14, 1895.

In a paper read before the Chemical Society in 1893, I showed that in the inner non-luminous zone of a flame of ordinary illuminating gas, the hydrocarbons originally present in the gas, and consisting of ethylene, butylene, benzene, methane, and ethane, became converted by the baking action of the walls of flame between which they had to pass into acetylene, and that at the moment when luminosity commenced, over 80 per cent. of the total unsaturated hydrocarbons present consisted of this compound.

The presence of acetylene at the point where luminosity commenced naturally suggested that it was in some way due to actions in which the acetylene played the principal part—either that it split up into carbon and hydrogen under the influence of heat, and so supplied the flame with the solid particles necessary, according to Sir Humphry Davy's theory of the cause of luminosity, or else by its polymerisation it formed the dense vapours required by Dr. E. Frankland's more recent hypothesis.

In order to elucidate this point, I carried out the long series of experiments upon the action of heat upon flowing ethylene and other hydrocarbons, which formed the subject of communications to the Royal Society in 1893 and early this year, in which I showed that whilst flowing through a heated area (the temperature of which was between 800° and 1000° C.), ethylene decomposed according to the equation

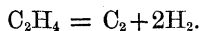


and that the acetylene then polymerised into a large number of more complex hydrocarbons, amongst which benzene and naphthalene were conspicuous, whilst at temperatures above 1200° C., no polymerisation

took place, but the acetylene formed from the ethylene decomposed at once into carbon and hydrogen, whilst the methane, which up to this temperature had been but little affected, decomposed into



and this fresh supply of acetylene at once broke up to carbon and hydrogen, so that at temperatures above 1200°C. the complete action might be looked upon as being



These results have an important bearing upon the cause of the luminosity in the flame, as it is manifest that if the temperature of the luminous zone is above 1200°C. , the light emitted must be due to incandescent particles of carbon, and not to incandescent hydrocarbon vapours.

On determining the temperature of an ethylene flame whilst burning from a small fish-tail burner by means of the Le Chatelier thermocouple, used in the way described in my paper* on the luminosity of coal-gas flames, I found that the temperatures were as follows:—

| Portion of flame. | Height above burner. | Temperature. |
|--------------------------------|----------------------|-----------------------|
| Non-luminous zone | $\frac{1}{2}$ inch. | 952°C. |
| Commencement of luminosity ... | $1\frac{1}{4}$ „ | 1340 |
| Top of luminous zone | 2 „ | 1865 |
| Sides of „ „ | | 1875 |

showing that luminosity commenced at 1340°C. , and continued even at 1875°C. , temperatures at which the incandescent vapour theory becomes untenable.

It might be urged that the heavy hydrocarbons already produced at a lower temperature in the non-luminous zone are not so easily decomposed by heat as acetylene, and that these may be causing the luminosity, even though carbon particles be present from the decomposed acetylene; but this would hardly be possible, as so little besides acetylene is to be found at the top of the non-luminous zone of an ethylene flame, and it can be experimentally shown that even when benzene vapour is formed and is largely diluted it begins to break up and deposit carbon at 1200°C.

The supporters of the “solid particle” theory of luminosity agree in concluding that the liberated carbon, existing as it does in a condition of molecular division, is heated to incandescence partly by its own combustion, and partly by the combustion of the hydrogen and carbon monoxide going on around the finely-divided carbon particles.

* ‘Chem. Soc. Journal,’ 1893.

As has been pointed out by many observers, it is clear that the carbon particles themselves undergo combustion, otherwise they would escape unburnt from the flame, whilst it is manifest that the combustion of hydrogen and carbon monoxide, which plays so important a part in the flame, must add its iota to the temperature attained by them.

Both these sources of temperature, however, would be manifest in the flame itself, and with flames of given size burning from the same description of jet we ought to find that their luminosity is governed by—

A. The temperature of the flame.

B. The number of carbon particles in a given area.

Moreover, we should expect that the higher the temperature of the flame, the whiter would be the light emitted, so that a comparatively low temperature flame, even when rich in carbon particles, would be yellow and lurid as compared with a flame containing the same or a smaller number of particles, but which had a higher temperature.

It has been pointed out by Professor A. Smithells* that it is erroneous to consider the temperature of a flame as being the temperature recorded by thermometric instruments inserted into the flame, as by such devices you only obtain the mean temperature of a considerable area of the flame uncorrected for loss from conduction.

It is also perfectly well known that in a flame a thick platinum wire may only be heated to redness, whilst a thin wire may even be fused, and this suggests that flame temperatures taken by the Le Chatelier thermo-couple of platinum and platinum-rhodium wires may be totally incorrect. In using this beautiful and convenient device, I have found that the length of the wires twisted together made practically no difference in the recorded temperature, and that one twist was as good as six.

In all my flame experiments I have made the twist as short as possible, and by always using wires of the same thickness have obtained results which are at any rate comparable if not correct, and in order to find what difference the thickness of the wires would make, I got Messrs. Johnson and Matthey to draw for me wires of 0·018, 0·011, and 0·003 of an inch diameter, and having calibrated the galvanometer scale for temperature with thermo-couples of the same length of twist made from each of them, obtained the following results with the same portion of a Bunsen flame.

| Wire used. | Temperature shown. |
|------------|--------------------|
| 0·018 | 1617° C. |
| 0·011 | 1728 |
| 0·003 | 1865 |

* 'Phil. Mag.,' 1894, p. 249.

These results show that the diameter of the wire seriously affects the temperature recorded under these conditions by the thermo-couple, the same degree of heat being recorded by the fine wire as being 248° hotter than is shown by the thickest wire employed, this discrepancy being probably chiefly due to loss by conduction.

In taking the temperature of heated gas flowing through a tube this source of error is but small, as some considerable length of wire being heated on each side of the twist, conduction has but little effect on the thermo-couple itself, but in determining the temperature of flames it is manifest that the finest usable wire must be employed in order to reduce the error from conduction. Test experiments also showed that no part of the thermo-couple must project beyond the flame, as if it did a considerable diminution in the recorded temperature took place.

For these reasons it was manifestly best to use the finest wire which could be employed without the risk of fusing at the temperatures existing in the flames to be tested; and all temperatures recorded in this paper were made with wire 0.011 in. in diameter, the twist being as short as possible, so that it is probable that, although the temperatures may be from 100° to 200° too low, yet the results are strictly comparable.

Experiments which I have lately made with pure acetylene, prepared by the action of water upon calcic carbide, show it to be the most powerful illuminant to be found amongst the gaseous hydrocarbons, as when burnt in a small flat flame burner under the most suitable pressure, and its illuminating power calculated to a flow of 5 cubic ft. an hour, its value is equal to about 240 candles.

The colour of the flame is pure white, and an ethylene flame beside it looks yellow and dull—the purity of the light at once suggesting a very high condition of incandescence in the particles of carbon present in the flame.

On now taking the temperature of the various portions of the flame, and comparing these with the temperatures obtained in the same way with the ethylene flame and a coal-gas flame of the same size, the following results are obtained:—

| Portion of flame. | Acetylene. | Ethylene. | Coal gas. |
|--------------------------------|------------------|------------------|-------------------|
| Non-luminous zone | 459° C. | 952° C. | 1023° C. |
| Commencement of luminosity.. | 1411 | 1340 | 1658 |
| Near top of luminous zone | 1517 | 1865 | 2116 |

whilst the illuminating values of the gases calculated to a flow of 5 cubic ft. an hour in the burners best suited for their consumption, are

| | |
|-----------------|-------|
| Acetylene | 240.0 |
| Ethylene | 68.5 |
| Coal gas..... | 16.8 |

whilst if all were compared when burning from flat-flame burners of the same size as those in which the temperatures were determined, the results when calculated to a consumption of 5 cubic ft. an hour would be

| | |
|---------------------|-------|
| Acetylene | 211.0 |
| Ethylene | 31.5 |
| Coal gas | nil |

Here then we have the anomaly of three gases, which not only do not conform to the preconceived expectation, but which have their ratio of temperature and illuminating value directly opposed to each other.

In the case of the acetylene and ethylene, moreover, the molecules contain the same number of atoms of carbon, and yet we obtain so enormous a discrepancy in their illuminating value.

The fact that there is no apparent relation existing between the temperature of the flame, or the probable number of carbon particles contained in it and its illuminating value, at once suggests that the luminosity must be in great part governed by some thermo-chemical changes taking place in the flame itself, and which do not of necessity affect the average temperature of the flame to any great degree.

The researches of Hittorf* and Siemens show that air, steam, and the oxides of carbon, even when heated to temperatures above those existing in luminous hydrocarbon flames, are perfectly non-luminous, and the fact that the Bunsen flame, when supplied with sufficient air, has a temperature exceeding 1800° C. in its hottest part, and yet emits no light, shows us that it is exceedingly unlikely that any interactions leading to luminosity take place amongst these ordinary flame gases.

The fact that most of the unsaturated hydrocarbons in the flame are converted into acetylene before luminosity commences, naturally draws one's attention to this body, and the fact that it is highly endothermic, at once suggests the idea that it may be the liberation of heat during its decomposition that endows the carbon particles produced from it with an incandescence far higher than any which could be expected from the temperature of the flame.

Berthelot has calculated that the temperature developed by the detonation of acetylene at constant volume is no less than 6220° C., and if this be imparted at the moment of its liberation to the products of its decomposition, the incandescence of the carbon particles is at once explained.

If luminosity be even partly due to this cause, the detonation of pure acetylene first recorded by Berthelot should develop light. In order to see if this were so, a thin glass tube, closed by a cork, had

* 'Wied. Ann.,' vol. 7, pp. 587, 591.

a detonator containing one-tenth of a gram of mercuric fulminate suspended in it by two copper wires, which were connected by a thin platinum wire in contact with the fulminate, and on firing the detonator by the electric current the flash of the fulminate was found to emit but a feeble light.

The same charge was fixed in a similar tube filled with pure acetylene collected over mercury, the result being a flash of intense white light and the shattering of the tube, the pieces of which were thickly coated with the carbon produced by the decomposition of the acetylene.

Moreover, the small piece of white tissue paper used to contain the fulminate was only scorched at the points where the explosion of the fulminate had burst through it, showing that in the instantaneous decomposition which had taken place, the intense heat which had been developed either was confined to the products of decomposition, or else had not had time to scorch the paper.

The experiment at first sight seemed conclusive evidence that it was the endothermic nature of the acetylene which, during its decomposition in the flame, endowed the particles of carbon with the necessary incandescence, but the objection presented itself that, when exploding mixtures of oxygen and hydrogen in the eudiometer, a distinctly luminous flash is produced, and, although the light so obtained is feeble as compared with the intensity of the white light produced by the detonation of the acetylene, still further proof is necessary before this action can be accepted as the prime factor in producing luminosity.

It is also manifest that it would not do to assume that the rapidity of the decomposition of the acetylene in a flame was nearly so great as when the undiluted gas was detonated, and the question arose as to whether it would be possible to obtain evidence as to acetylene, when exposed to heat alone, liberating carbon in a luminous condition.

Although the instantaneous liberation of heat on the decomposition of the gas by detonation appears to confine the temperature to the products of its decomposition, it was to be expected that, on being decomposed by heat, and probably, therefore, at a slower rate, the increase in temperature might be detected.

To try this, pure acetylene was passed through a platinum tube 2 mm. in diameter and 40 cm. long, in which the Le Chatelier thermo-couple was arranged as follows:—The two wires were twisted together for a length of 3 mm., and the wires on either side of the twist are then passed through thin glass tubes, which are fused on to them; having been in this way coated with glass so that only the twist is exposed, they are passed through the platinum tube, the glass insulating the wire from the metal of the tube, and also keeping

the thermo-junction in such a position that it registers the temperatures of the gas in the tube, not that of the wall of the tube. To each end of the platinum tube glass T-pieces are fitted, down the stems of which the wires pass to mercury seals; from the metal seals conducting wires lead to the resistance coils, the key, and a reflecting galvanometer.

A steady flow of acetylene was allowed to pass through the tube, and was led into water at the other end. The tube was slowly and carefully heated for about 4 in. of its length, and, as the temperature reached 700°C ., white vapours began to flow from the tube, and these, as the temperature rose, increased in quantity. The source of heat had been so regulated that the temperature had risen about 10° per minute, but, almost immediately 800°C . was passed, the galvanometer registered a sudden leap up in temperature to about 1000°C ., whilst finely-divided carbon poured from the tube. This seemed to indicate that 800° was about the temperature at which the pure acetylene broke up into its constituents, and an experiment was now made to see if this developed incandescence in the liberated carbon.

A small glass combustion tube was well supported, and heated to the highest temperature attainable with one of Fletcher's big blow-pipes, whilst pure acetylene was slowly flowing through it, the heating not being commenced until the tube was filled with the pure gas, all air being thoroughly rinsed out. As the temperature reached the softening point of the glass, the acetylene apparently burst into a lurid flame at the point where it entered the zone of heat, and clouds of carbon swept forwards through the tube; but, although the carbon particles had to traverse an inch or more of tube more highly heated than the point of entering the hot zone, it was only at this latter point that the luminosity was developed, proving beyond doubt that it was the heat evolved by the decomposition, and not the external heating, which caused the carbon particles to emit light.

If it is the decomposition of the molecule of acetylene which develops the heat which is the cause of the incandescence of the carbon particles, then, if acetylene could be burnt without decomposition, a non-luminous flame should be produced. It is conceivable that this might be done by so diluting the acetylene that it would require a much higher temperature to break it up.

It was Heumann who showed* that hydrocarbon gases may burn with luminous flames, *i.e.*, with separation of carbon in the flame, or with non-luminous flames, *i.e.*, without any separation of carbon, and that the maintenance of a high temperature is an essential condition of luminosity: a flame, the temperature of which has been lowered by any means, being no longer able to bring about the required

* 'Liebig's Annalen,' vol. 183, Part I, pp. 102—131.

separation of carbon. He also points out* that "combustible matter, when diluted with indifferent gases, requires to be maintained at a higher temperature, in order that it may burn with a luminous flame, than when it is undiluted with such gases."

Dr. Percy Frankland, in his researches on the effect of diluents upon the illuminating value of hydrocarbons,† showed that ethylene, which was capable of developing a light of 68·5 candles power when burnt by itself, became non-luminous when diluted with about:—

| | |
|-----------------------|--------------|
| Hydrogen | 90 per cent. |
| Carbon monoxide | 80 ,, |
| Carbon dioxide | 60 ,, |
| Nitrogen | 87 ,, |

results which all show that excessive dilution by inert gases destroys luminosity.

In order to see if dilution had the same effect upon acetylene, experiments were made by diluting it with pure hydrogen. The gases were mixed over water, the proportion of acetylene actually present in the gas being determined by analysis at the burner, and although the water in both holder and meter was, as far as possible, saturated with the gas, yet, as the analyses show, the precaution was an important one.

| Composition of mixture. | | | | Illuminating value of mixture per 5 c.c. when burnt in 00 Bray. |
|-------------------------|------------|------------|------------|--|
| Made in holder. | | At burner. | | |
| Hydrogen. | Acetylene. | Hydrogen. | Acetylene. | |
| 90 | 10 | 90·5 | 9·5 | nil |
| 80 | 20 | 81·5 | 18·5 | 1·8 |
| 70 | 30 | 65·5 | 34·5 | 14·0 |
| 50 | 50 | 43·5 | 56·5 | 87·0 |

Showing that dilution with between 80 and 90 per cent. of hydrogen rendered the acetylene non-luminous when the mixture was burnt from a burner suitable for the higher values of gas.

In order to determine the point at which luminosity was destroyed when consuming the mixture in a burner suited to develop the light from a gas of low illuminating power, the experiment was repeated, using a 3-in. flame burning from the London argand, and also from a No. 4 Bray union jet, the latter being employed as it is difficult to determine the temperature in the argand flame.

* 'Liebig's Annalen,' vol. 183, Part I, pp. 102—131.

† 'Chem. Soc. Jour.,' vol. 45, p. 30 and p. 227.

| Analysis of mixture. | | Illuminating value per 5 cub. ft. | |
|----------------------|------------|--------------------------------------|-------------|
| Hydrogen. | Acetylene. | Argand. | No. 4 Bray. |
| 92 | 8 | Not measurable | |
| 91 | 9 | Not measurable | |
| 88.5 | 14.5 | 4.1 | 1.7 |

so that luminosity would be destroyed in the argand by dilution with about 90 per cent. hydrogen, and in the No. 4 Bray with about 88 per cent.

The next point to be determined was whether the destruction of luminosity in the diluted acetylene flame was in reality due to dilution rendering it necessary to employ a higher temperature for the decomposition of the acetylene, or to other causes.

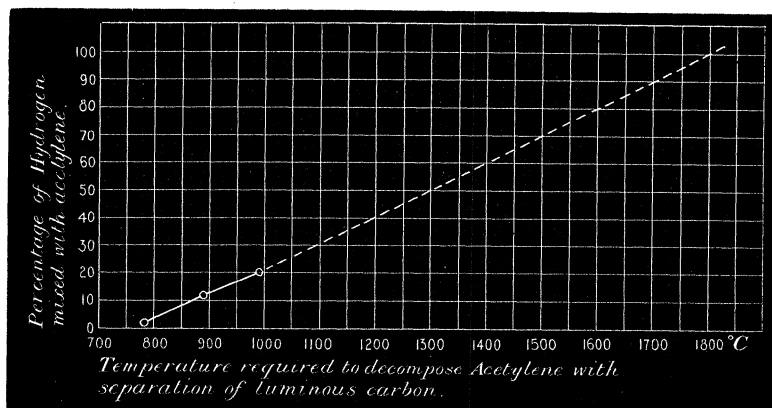
In order to do this, a tube made of specially infusible glass 4 mm. in diameter was taken, and the Le Chatelier thermo-couple was fitted into it in the same way as before, used with the platinum tube, and all air having been rinsed out by a current of the mixture to be experimented with, the gas was allowed to pass at a steady rate of flow through the tube, the point at which the thermo-couple was situated being steadily heated by the Fletcher blowpipe, whilst the temperature recorded on the scale was noted the moment that incandescent liberation of carbon commenced.

| Percentage composition of gas. | | Temperature necessary to cause deposition of carbon with luminosity. |
|--------------------------------|-----------|--|
| Acetylene. | Hydrogen. | |
| 100 | 0 | 780° C. |
| 90 | 10 | 896 |
| 80 | 20 | 1000 |

It was found impossible to obtain a glass tube which would stand temperatures higher than this; but on plotting out the points so obtained, and which give a fairly straight line, it is seen that even if the increase in temperature only continues for increased dilution in the same ratio as shown in the experimental determinations, which is extremely unlikely, the reason of the destruction of luminosity in highly-diluted hydrocarbon gases is at once explained, as an increase of each 10 per cent. in the dilution would necessitate an increase of 100° C. in the temperature of the flame, and with 90 per cent. dilution a temperature of over 1700° C. would be required to bring about decomposition.

My reason for believing that it is highly improbable that when dilution is great it only requires the same increment in temperature to bring about decomposition as when the dilution is small, is that in all the work I have done on the effect of diluents upon luminosity, and also in Professor Percy Frankland's researches upon the same

FIG. 1.



subject, dilution with hydrogen and carbon monoxide acts regularly, and decreases the value of the illuminant in a direct ratio down to about 50 per cent., whilst when the degree of dilution exceeds 60 per cent. a rapid falling away in the luminosity takes place, a fact which I think points clearly to a regular *pro rata* rise of temperature being needed for increase in dilution up to between 50 and 60 per cent., whilst higher degrees of dilution need a far greater rise of temperature in order to bring about decomposition.

Moreover it would be manifestly incorrect to look upon the percentage of acetylene present in the gas issuing from the burner as being any guide to the degree of dilution existing at the point at which luminosity commences. As the two small streams of gas issuing from the holes in the union jet meet and splay themselves out into the flat flame, they draw in with them a considerable proportion of air, the quantity being governed by the pressure of the gas at the burner.

This can be clearly seen by the fact that a high value gas which burns from a union jet burner of a given size with a smoky flame, under a gas pressure of half an inch of water, will burn with a bright, smokeless, and rigid flame of greatly increased illuminating value when the pressure is raised to 2 in., whilst an ordinary coal gas of 16-candle value must be burnt from a flat flame burner at a pressure of about 0.75 in. if the best results are to be obtained, the increase in air drawn in, if the pressure rises to a much higher degree, diminishing the illuminating value.

Then, again, the area of non-luminous combustion in a mixture of gases like coal gas means that some at least of the hydrocarbons are consumed before the required temperature for their decomposition is

reached, whilst the products of combustion formed in the lower part of the flame are mixed with the flame gases, partly by diffusion and partly by being drawn into it by the upward rush.

When a simple hydrocarbon like ethylene or acetylene is burnt alone, the whole of the heat required to bring about the decomposition has to be generated by the combustion, without decomposition, of a considerable proportion of the hydrocarbon, and this means considerable dilution at the spot where the luminosity commences, so that at the top of the non-luminous zone of an acetylene flame there is only some 14 or 15 per cent. of acetylene present, diluted with nitrogen, hydrogen, water vapour, and the oxides of carbon, whilst, with a mixture of 10 per cent. acetylene and 90 per cent. of hydrogen, in some cases little or no acetylene could be found at the top of the inner zone of the flame, it either having diffused with the hydrogen and been consumed, or polymerised to other compounds.

It is manifest that the luminosity of a flame will be governed, not by the percentage of acetylene in the gas, but at the point at which the temperature is sufficiently high to bring about decomposition.

If, instead of making a mixture of 90 per cent. hydrogen and 10 per cent. acetylene, the hydrogen is burnt at the end of an open platinum tube, which has a fine platinum tube passing up the centre to the top of the inner zone of the flame, and if the acetylene be passed into the flame at the rate of one volume for every ten of the hydrogen, not only do we obtain an intensely luminous, but a very smoky flame.

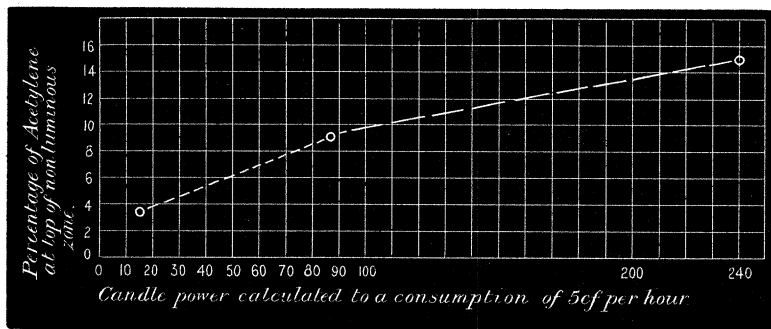
In this experiment the gases were issuing from their respective tubes at the same pressure, but the small tube soon choked from deposited carbon, and it was found that the same results could be equally well attained by drawing down the inner tube to the level of the hydrogen tube, and making the acetylene issue at a slightly higher rate of flow, which hurried it in a compact stream through the inner zone of the hydrogen flame.

In order to see if the percentage of acetylene present at the top of the non-luminous zone bore any ratio to the illuminating value of the mixture, experiments were made in which mixtures of hydrogen and acetylene were burnt at a small flat flame burner, and the percentage of acetylene was determined by gently aspirating out some of the flame gases from the top of the non-luminous zone.

| Analysis of mixture used. | | Acetylene at top of non-luminous zone. | Illuminating value of flame for 5 cub. ft. |
|---------------------------|------------|--|--|
| Hydrogen. | Acetylene. | | |
| 65.5 | 34.5 | 3.72 | 14.0 |
| 43.5 | 56.5 | 8.42 | 87.0 |
| 0.0 | 100.0 | 14.95 | 240.0 |

On plotting out these results, they certainly seem to point to the fact that, with flames of the same size burning from the same burner, the light emitted by the flame is directly proportional to the percentage of acetylene present at the top of the non-luminous zone of the flame, provided always that the temperature is sufficiently high to complete its decomposition.

FIG. 2.



It is perfectly possible for the temperature of a flame to be so little above the point necessary to decompose the diluted acetylene that, whilst some decomposes and renders the flame faintly luminous, the larger portion burns without decomposition. A good example of this is to be found in the combustion of alcohol, the flame of which contains as much acetylene as is to be found in a good coal-gas flame, but which is practically almost non-luminous. If alcohol in a small dish be ignited, it burns with a faintly luminous flame, and if a bell-jar is placed over it, some of the products of combustion mingling with the flame still further cool it and render it non-luminous; but if now a stream of oxygen be introduced under the bell-jar the temperature of the flame is at once increased and becomes highly luminous, whilst a cold porcelain vessel held in the flame is coated with soot.

In all the experiments in which light was developed in heated tubes by the decomposition of acetylene, the glow of the carbon was red and lurid, the light emitted being of the same character and appearance as that developed by the combustion of potassium in carbon dioxide, and entirely lacking the pure white incandescence of the acetylene flame as burnt from a flat-flame burner.

This may be due to the fact that in the open flame the temperature of the carbon particles is presumably due to three sources of heat:—

- A. Heat derived from the decomposition of the acetylene molecule.
- B. Heat derived from the combustion of hydrogen, carbon monoxide, and some hydrocarbons in the flame.
- C. Heat derived from the combustion of the carbon particles themselves,

whilst in the tube experiments the heat of the walls of the tube and the heat of decomposition alone are acting, and it is evident that the intensity of the heat finding its way through the walls of the tube will be very different to that exercised by the walls of burning gas which enclose the luminous portion of the flame, and there can be but little doubt that the temperature of the carbon particles will vary enormously with the rate at which the acetylene decomposes, as the more quickly the action takes place, the greater will be the localising action upon the heat evolved, and the higher the incandescence of the carbon particles.

That this is so seems certain from the whiteness of the flash of light emitted when the acetylene is detonated, and experiments were made in order, if possible, to gain an idea as to how much of the incandescence of the carbon particles was due to the endothermicity of the decomposing acetylene, and how much to the action of heat and combustion on the carbon particles after formation.

In order to do this, a non-luminous flat flame of large size was desired, and was obtained by using coal gas de-illuminated by slowly passing it through bromine, well washing with sodic hydrate solution and water, and then passing it through strong sulphuric acid, the gas so treated having an illuminating value of 1·2 candles for 5 cubic feet when burnt in the London argand at such a rate as to give a 3-in. flame, whilst in a fish-tail burner it gave a non-luminous flame. This gas gave on analysis the following percentage composition :—

| | |
|-----------------------------|--------|
| Carbon dioxide | 0·00 |
| Unsaturated hydrocarbons .. | 0·00 |
| Carbon monoxide | 5·50 |
| Saturated hydrocarbons..... | 33·28 |
| Hydrogen..... | 55·25 |
| Nitrogen | 5·49 |
| Oxygen..... | 0·48 |
| | <hr/> |
| | 100·00 |

so that its combustion would give practically the same temperature and flame reactions as those in an ordinary gas flame.

A very fine platinum tube was now obtained, closed at one end, and with five minute holes bored in a line close to the sealed end, and

this having been so arranged that the holes were buried in the flame just at the top of the inner zone, acetylene was then gently allowed to flow through them into the flame.

At the points where the acetylene issued into the flame, small areas of intense luminosity were produced, whilst the liberated carbon streaming up between the flame walls of the upper zone produced dull red bands of very low luminosity. It may be suggested that the carbon particles supplied in this way to the flame may have agglomerated and formed masses larger than those produced in the ordinary way, but I do not think this, as they were completely consumed, and no smoke escaped from the crown of the flame, whereas if a flat flame is interfered with in such a way as to cause the carbon particles to roll themselves together, smoking of the flame is produced.

I think the inference to be drawn from this experiment undoubtedly is that it is the heat of decomposition which gives the high incandescence and light emitting value to the carbon particles, and that the temperature of the combustion of the other flame gases and finally of the carbon itself plays but a secondary part.

In considering these results, it seems remarkable that if acetylene owes its power of rendering hydrocarbon flames luminous to its high endothermic properties, that cyanogen, which is still more endothermic, should burn under all conditions that have at present been tried with a non-luminous flame.

Heat of formation.

| | | |
|-----------------|----------|---------|
| Acetylene | C_2H_2 | —47,770 |
| Cyanogen | C_2N_2 | —65,700 |

It is clear that if the rapidity of decomposition localises the heat evolved to the products of decomposition, and that this renders the liberated carbon particles incandescent, whilst the hydrogen plays at best a very subsidiary part, it ought not to matter whether it be hydrogen or nitrogen which is combined with the carbon.

Berthelot showed that cyanogen like acetylene could be detonated by a small charge of mercuric fulminate, but he notes that the test is not always successful, which points to the decomposition of this body requiring a greater expenditure of energy to break up the molecule than is the case with acetylene, and known facts would lead us to expect that this would be the case, as although exothermic compounds become less and less stable with rise of temperature, endothermic bodies on the other hand become more stable, and the endothermicity of cyanogen being greater than that of acetylene, would lead one to expect that temperatures which would decompose acetylene would have no effect on cyanogen, and that, as during the combustion of cyanogen, the liberation of nitrogen

would probably have a diluting and cooling action, the cyanogen would burn directly without liberating any carbon which could emit light.

In order to see if the temperature of the cyanogen flame when burnt from an ordinary flat flame burner differed much from that of hydrocarbons when consumed in a flame of the same size and kind, the temperatures were experimentally determined by the same method employed, and in the same parts of the flame as had before been done with acetylene, ethylene, and coal gas.

| Portion of the flame. | Temperature. |
|------------------------------|--------------|
| Centre of inner zone | 1377° C. |
| Top of inner zone | 2085 |
| Near top of outer zone | 1645 |

Showing that the cyanogen flame was actually hotter than the acetylene and ethylene flames, and about the same as the coal gas flame, but that the heat was differently distributed, the inner zone being far hotter than in the other gases, whilst the maximum temperature of the flame was at the apex of the inner zone, instead of being nearer the top of the flame.

An experiment was now made to ascertain if it were possible to decompose cyanogen with luminous deposition of carbon, by passing it through a hard glass tube heated by means of the blowpipe; but at the highest temperature attainable no trace of any deposition of carbon took place, showing how far more stable cyanogen is under the influence of high temperatures than acetylene.

The structure and characteristic appearance of the cyanogen flame have been explained by Smithells* and Dent, who conclude that the inner zone of peach blossom tint is caused by the combustion of the cyanogen to carbon monoxide and nitrogen, whilst the outer blue cone is formed by the oxidation of the monoxide to dioxide, the green fringe to the outer cone being attributed to the presence of small quantities of oxides of nitrogen; and if this explanation be accepted, it is clear that we could not obtain luminosity in the portion of the flame immediately above the inner zone, as all cyanogen has been destroyed without decomposition before that point is reached. It is conceivable, however, that although no luminosity can be detected in a cyanogen flame, and although the temperature which can be obtained in a glass tube is insufficient to break up the compound with luminous separation of carbon, yet if cyanogen could be heated to a considerably higher temperature, it might be possible to decompose it in such a way as to develop luminosity.

In order to try this point, a hydrogen flame was burnt from the end of an open platinum tube 9 mm. in diameter, and a thin platinum

* 'Chem. Soc. Jour.,' 1894, p. 603.

tube 2.5 mm. in diameter was passed up through the broad tube to the apex of the inner zone, and a slow stream of cyanogen was admitted, with the result that the flame at once became luminous, and on surrounding the hydrogen flame with an atmosphere of oxygen to increase the temperature, the luminosity was considerably increased.

This experiment at once explains the cause of the non-luminosity of the cyanogen flame, and shows that it is purely a question of temperature, and the probabilities are that, burnt in a flame which gave sufficient heat to rapidly decompose it, nearly as high an illuminating value as that of acetylene would be obtained.

I think the explanation of the apparent anomaly of the cyanogen flame having a higher temperature than the acetylene and ethylene flames, is to be found in the fact that the molecules of cyanogen are consumed without previous decomposition, so that the heat absorbed during the formation of the cyanogen is added to the heat of combustion, and raises the average temperature of the flame, whereas with acetylene the instantaneous decomposition of the molecule before combustion confines the heat evolved to the liberated products, and the average temperature of the flame is but little more than the heat of combustion.

If the luminosity of a hydrocarbon flame is principally due to the localisation, during intensely rapid decomposition, of the heat of formation in the products, the illuminating values of such hydrocarbon gases as contain two atoms of carbon in the molecule should bear a simple ratio to their heat of formation. The gaseous hydrocarbons are—

| Hydrocarbon. | Composition. | Heat formation at constant pressure. |
|-----------------|--------------|--------------------------------------|
| Ethane | C_2H_6 | +25670 |
| Ethylene | C_2H_4 | — 8000 |
| Acetylene | C_2H_2 | —47770 |

and although they may undergo many changes in the flame, they will all ultimately be reduced to carbon and hydrogen again before the full luminosity of the flame is developed.

When the acetylene into which these hydrocarbons is converted by heat is decomposed, the action takes place with such enormous rapidity that one would expect the heat evolved to simply divide itself amongst the liberated atoms, so that the question of specific heat at high temperatures may be omitted.

With exothermic compounds like ethane, considerable heat will have to be developed by its own combustion before it is converted into the acetylene, which, by its decomposition, endows the flame with luminosity, and if we take the ethane and call its light producing energy 1, we can then obtain a ratio of such energy for the

other hydrocarbons available for distribution amongst the products of decomposition.

| | | |
|-----------------|-----------------------------|--------|
| Ethane | $\frac{25670}{25670}$ | = 1 |
| Ethylene..... | $\frac{25670+8000}{25670}$ | = 1.31 |
| Acetylene | $\frac{25670+47770}{25670}$ | = 2.86 |

These ratios must now be divided amongst the atoms liberated at the moment of decomposition from the molecule, and we thus obtain the ratio :—

$$\begin{array}{ccc} \text{C}_2\text{H}_6. & \text{C}_2\text{H}_4. & \text{C}_2\text{H}_2. \\ \frac{1}{8} & : \frac{1.31}{6} & : \frac{2.86}{4} \end{array}$$

or

$$1 : 1.74 : 5.72$$

The determination of the illuminating value of a gas becomes more and more difficult the higher its illuminating value, owing to the cooling effect of the small burners that must of necessity be used in order to ensure complete combustion. Dr. Percy Frankland* assigned the illuminating value of 35 candles to ethane as the mean of four tests, which varied considerably amongst themselves, and, adopting his figure, the calculated illuminating values for the ethane, ethylene, and acetylene would be :—

| | Illuminating value. | |
|-----------------|--------------------------|--------|
| | Calculated. | Found. |
| Ethane | $1 \times 35 = 35$ | 35 |
| Ethylene..... | $1.79 \times 35 = 60.9$ | 68.5 |
| Acetylene | $5.72 \times 35 = 200.2$ | 240 |

figures which are far nearer the experimental ones than could have been expected, considering the crude character of the calculation and insufficient data, which leads to omitting altogether such important factors as the amount of gas consumed to bring about the requisite temperature of decomposition, the specific heat of the products, and the thermal value of the change from gaseous to solid carbon, and are of no value except as showing that a ratio does exist between heat of formation and illuminating value.

Methane is the only other gaseous hydrocarbon of which the heat of formation is known, it being + 21750, and as the molecule contains only 1 atom of carbon, 2 mols. have to be taken, and on calculating the probable illuminating value by the same method as was applied to the other hydrocarbons, we should have—

* 'Chem. Soc. Jour.,' vol. 47, p. 237.

$$\frac{25670 + \{25670 - (21750 \times 2)\} \times 35}{\frac{25670}{10 \times \frac{1}{8}}} = 8.4,$$

and the illuminating value, as determined by Mr. Lewis T. Wright, is 5.2; but here, again, we know by experiment that methane requires a very high temperature to bring about its conversion into acetylene and decomposition into carbon and hydrogen, and that a large portion of the gas must be burnt without decomposition to do this.

The facts which I have sought to establish in this paper are:—

1. That the luminosity of hydrocarbon flames is principally due to the localisation of the heat of formation of acetylene in the carbon and hydrogen produced by its decomposition.

2. That such localisation is produced by the rapidity of its decomposition, which varies with the temperature of the flame and the degree of dilution of the acetylene.

3. That the average temperature of the flame due to combustion would not be sufficient to produce the incandescence of the carbon particles within the flame.

In my paper on the action of heat upon ethylene, brought before the Royal Society this spring, I showed that the decomposition of ethylene into acetylene and simpler hydrocarbons was mainly due to the action of radiant heat, and was but little retarded by dilution, whilst I have shown in this paper that the acetylene so produced requires a considerable increase in temperature to bring about its decomposition when diluted, and it is possible with these data to give a fairly complete description of the actions which endow hydrocarbon flames with the power of emitting light.

When the hydrocarbon gas leaves the jet at which it is being burnt, those portions which come in contact with the air are consumed and form a wall of flame which surrounds the issuing gas. The unburnt gas in its passage through the lower heated area of the flame undergoes a number of chemical changes, brought about by the action of radiant heat emitted by the flame walls, the principal of which is the conversion of the hydrocarbons into acetylene, methane, and hydrogen. The temperature of the flame quickly rises as the distance from the jet increases, and a portion of the flame is soon reached at which the heat is sufficiently intense to decompose the acetylene with a rapidity almost akin to detonation, and the heat of its formation, localised by the rapidity of its decomposition, raises the liberated carbon particles to incandescence, this giving the principal part of the luminosity to the flame; whilst these particles, heated by the combustion of the flame gases, still continue to glow, until finally

themselves consumed, this external heating and final combustion adding slightly to the light emitted.

Any unsaturated hydrocarbons which have escaped conversion into acetylene before luminosity commences, and also any methane which may be present on passing into the higher temperatures of the luminous zone, become converted there into acetylene, and at once being decomposed to carbon and hydrogen, increase the area of the light-giving portion of the flame.

My thanks are due to Mr. F. B. Grundy for the help he has given me in the work entailed by this paper.

IV. "A possible Explanation of the two-fold Spectra of Oxygen and Nitrogen." By E. C. C. BALY, A.I.C., 1851 Exhibition Scholar in University College, London. Communicated by Professor RAMSAY, F.R.S. Received February 27, 1895.

(Abstract.)

The two spectra of oxygen are shown to be of a different nature. They behave differently, and reasons are given for their being in all probability the spectra of different gases. They may either be two spectra produced by different vibrations of the oxygen molecule, or they may be the spectra of two different modifications of oxygen, or the spectra of two distinct gases resulting from a dissociation of oxygen, a combination of which is called oxygen.

It appeared worth while to undertake experiments with a view of testing the last of these. Oxygen was sparked in an apparatus similar to that used by Professor J. J. Thomson in his experiments on the electrolysis of steam. Hollow platinum electrodes were used, each one of which was connected with a Sprengel mercury pump. In the first experiments, the distance between the electrodes was 35 mm., and the highest pressure compatible with the appearance of the two spectra was made the starting point of the experiments. In these first experiments it was 380 mm. The density of the oxygen before sparking was determined, and taken as a test of its purity. The fractions obtained from the anode and cathode were weighed, and the results are given. They follow the lines of J. J. Thomson's results, inasmuch as with long sparks a lighter fraction was obtained at the cathode, and with short sparks a heavier fraction. The fractions from the anode were not so definite as from the cathode, though the difference was in the right direction. The probable maximum error of weighing was 0.0001 gram. This meant exactly one in the second decimal place of the density obtained. The general accuracy of the results may be gauged from the densities of unsparked oxygen obtained.

FIG. 1.

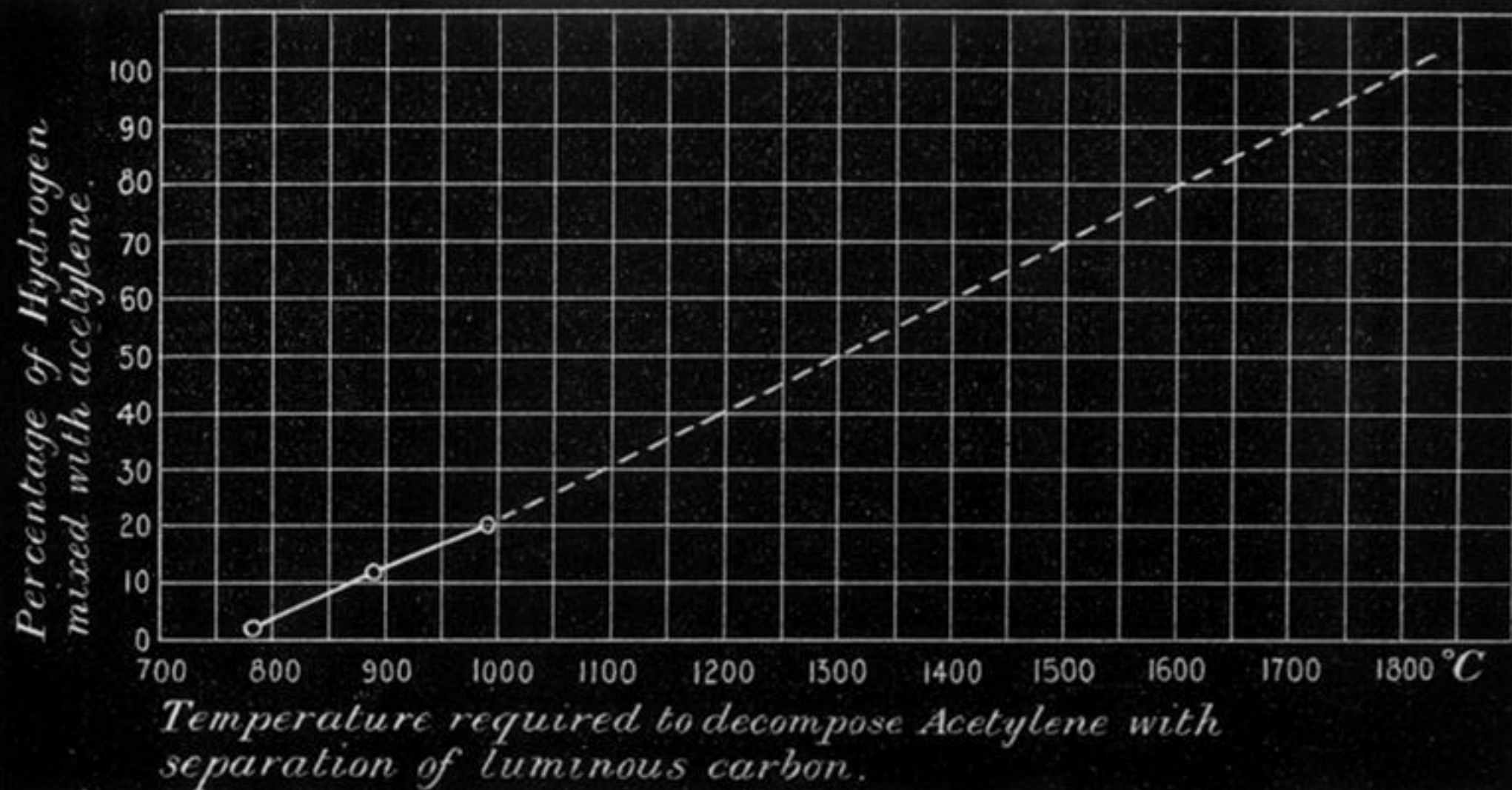


FIG. 2.

